This article was downloaded by: [Nova Southeastern University]
On: 31 December 2014, At: 09:40
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsrp20

Oxidation of organic sulfides by tetraethylammonium chlorochromate: a kinetic and mechanistic study

Deepika Sharma [a], P. Pancharia [a], K. Vadera [a] & Pradeep K. Sharma [a]

[a] Department of Chemistry, J.N.V. University, Jodhpur, 342 005, India

Published online: 08 Jun 2011.

To cite this article: Deepika Sharma, P. Pancharia, K. Vadera & Pradeep K. Sharma (2011) Oxidation of organic sulfides by tetraethylammonium chlorochromate: a kinetic and mechanistic study, Journal of Sulfur Chemistry, 32:4, 315-326, DOI: 10.1080/17415993.2011.587519

To link to this article: http://dx.doi.org/10.1080/17415993.2011.587519

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Journal of Sulfur Chemistry
Vol. 32, No. 4, August 2011, 315–326

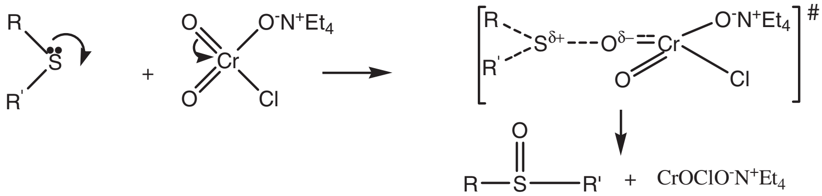
Oxidation of organic sulfides by tetraethylammonium chlorochromate: a kinetic and mechanistic study

Deepika Sharma, P. Pancharia, K. Vadera and Pradeep K. Sharma*

Department of Chemistry, J.N.V. University, Jodhpur 342 005, India

(*Received 27 March 2011; final version received 9 May 2011*)

The oxidation of organic sulfides by tetraethylammonium chlorochromate (TEACC) resulted in the formation of the corresponding sulfoxides. The reaction is first order with respect to both TEACC and the sulfide. The reaction is catalyzed by toluene-*p*-sulfonic acid (TsOH). The oxidation was studied in 19 different organic solvents. An analysis of the solvent effect by Swain's equation showed that both cation- and anion-solvating powers of the solvents play important roles. Correlation analyses of the rate of oxidation of 34 sulfides were performed in terms of various single and multiparametric equations. For the aryl methyl sulfides, the best correlation is obtained with Charton's *LDR* and *LDRS* equations. The oxidation of alkyl phenyl sulfides exhibited a very good correlation in terms of the Pavelich–Taft equation. The polar reaction constants are negative indicating an electron-deficient sulfur center in the rate-determining step. A mechanism involving the formation of a sulphenium cation intermediate in the slow step has been proposed.



Keywords: correlation analysis; halochromates; mechanism; oxidation kinetics; sulfides

1. Introduction

Pyridinium and quinolinium halochromates have long been used as mild and selective oxidizing reagents in the synthetic organic chemistry (*1–5*). Tetraethylammonium chlorochromate (TEACC) is one such compound used for the oxidation of primary aliphatic alcohols (*6*). There are very few reports investigating the oxidation kinetics of sulfides with TEACC (*7*, *8*). In contrast, there are many reports on the oxidation of sulfides by Cr(VI) reagents (*9*). For example, Karunakaran *et al.* (*10*) have reported a common mechanism for the oxidation of diphenyl sulfide by various Cr(VI) reagents in acetic acid. In the present article, we report the kinetics of oxidation of thirty-four

---

*Corresponding author. Email: drpkvs27@yahoo.com

ISSN 1741-5993 print/ISSN 1741-6000 online

DOI: 10.1080/17415993.2011.587519
http://www.informaworld.com

organic sulfides by TEACC in dimethylformamide (DMF) as a solvent. The objectives of this work are two-fold. First to find out if TEACC behave differently from other Cr(VI) reagents and secondly to study the effect of structure and solvent on the rate.

2. Results

The oxidation of organic sulfides by TEACC resulted in the formation of the corresponding sulfoxides. The overall reaction may be represented as Equation (1)

$$\mathrm{R-S-R' + O_2CrClO^-}N^+Et_4 \longrightarrow \mathrm{R-\underset{\|}{S}-R' + OCrClO^-N^+Et_4}. \tag{1}$$

TEACC undergoes a two-electron change. This is in accord with the earlier observations with TEACC (*7*, *8*) and with structurally similar halochromates (*9*). It has already been shown that both pyridinium fluorochromate (PFC) (*11*) and pyridinium chlorochromate (PCC) (*12*) act as two electron oxidants and are reduced to chromium (IV) species by determining the oxidation state of chromium by magnetic susceptibility, electron spin resonance and IR studies.

2.1. *Rate law*

Methyl phenyl sulfide was taken as a typical representative for detailed study. The reactions were found to be first order with respect to TEACC. The individual kinetic runs were strictly first order in TEACC (Figure 1). Further, the first-order rate coefficients did not vary with the initial concentration of TEACC. The order with respect to sulfide was also found to be one (Table 1). The experimental rate laws may be expressed as follows:

$$\frac{-\mathrm{d[TEACC]}}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{TEACC}] \tag{2}$$

$$\frac{-\mathrm{d[TEACC]}}{\mathrm{d}t} = k_2[\mathrm{TEACC}][\mathrm{sulfide}]. \tag{3}$$

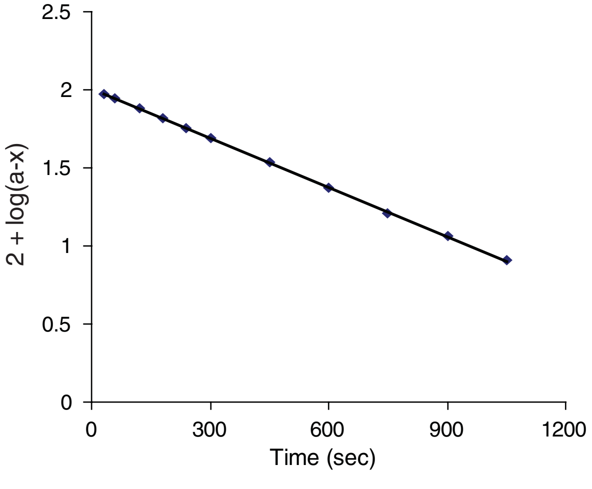


Figure 1. Oxidation of methyl phenyl sulfide by TEACC: a typical kinetic run.

Table 1. Rate constants for the oxidation of methyl phenyl sulfide by TEACC at 298 K.

10^3[TEACC] (mol dm^{-3})	[MeSPh] (mol dm^{-3})	[TsOH] (mol dm^{-3})	$10^4\ k_{\text{obs}}$ (s^{-1})	$10^3\ k_2$ (dm^3 mol^{-1} s^{-1})
1.0	0.10	0.0	2.65	2.65
1.0	0.20	0.0	5.26	2.63
1.0	0.40	0.0	10.8	2.70
1.0	0.60	0.0	16.2	2.70
1.0	0.80	0.0	21.1	2.64
1.0	1.00	0.0	26.1	2.61
2.0	0.20	0.0	5.58	2.79
4.0	0.20	0.0	4.86	2.43
6.0	0.20	0.0	5.09	2.55
8.0	0.20	0.0	4.59	2.29
1.0	0.40[a]	0.0	11.7[a]	2.92

Note: [a]Contained 0.001 mol dm^{-3} acrylonitrile.

2.1.1. *Test for free radicals*

The oxidation of methyl phenyl sulfide, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. It was observed that added 2,6-di-*t*-butyl-4-methylphenol was recovered

Table 2. Rate constants and activation parameters of the oxidation of organic sulfides by TEACC.

	$10^4\ k_2$ (dm^3 mol^{-1} s^{-1})				ΔH^*	ΔS^*	ΔG^*
Substituents	288 K	298 K	308 K	318 K	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}
(i) Aryl methyl sulfides							
H	9.45	26.1	65.7	171	70.6 ± 0.7	−58 ± 2	87.8 ± 0.5
p-Me	19.1	51.3	126	306	67.8 ± 0.3	−62 ± 1	86.1 ± 0.2
p-Ome	41.4	108	252	612	65.4 ± 0.6	−64 ± 2	84.3 ± 0.5
p-F	10.8	28.8	73.8	189	70.0 ± 0.7	−59 ± 2	87.5 ± 0.5
p-Cl	6.57	18.9	49.5	133	73.5 ± 0.7	−51 ± 2	88.6 ± 0.5
p-NO_2	0.63	2.00	5.94	18.0	82.3 ± 0.8	−40 ± 3	94.1 ± 0.7
p-COMe	1.44	4.50	12.6	36.0	77.1 ± 0.6	−45 ± 2	92.1 ± 0.5
p-COOMe	2.07	6.30	17.1	48.6	77.1 ± 0.8	−48 ± 3	91.3 ± 0.6
p-Br	6.39	18.0	48.3	130	73.8 ± 0.7	−50 ± 2	88.6 ± 0.5
p-NHAc	20.7	56.7	135	342	68.1 ± 0.8	−60 ± 3	85.9 ± 0.6
p-NH_2	135	324	720	1620	60.3 ± 0.5	−72 ± 1	81.5 ± 0.4
m-Me	17.1	45.0	108	270	67.1 ± 0.7	−65 ± 2	86.4 ± 0.5
m-Ome	19.8	52.2	126	306	66.7 ± 0.5	−65 ± 1	86.1 ± 0.5
m-Cl	3.45	10.4	26.4	71.1	73.7 ± 0.8	−56 ± 3	90.1 ± 0.4
m-Br	3.42	9.90	26.1	70.2	73.9 ± 0.6	−55 ± 2	90.2 ± 0.5
m-I	4.14	11.7	30.6	81.0	72.7 ± 0.6	−58 ± 2	89.7 ± 0.5
m-NO_2	0.41	1.31	3.87	11.7	82.2 ± 0.8	−44 ± 3	89.7 ± 0.6
m-CO_2Me	1.80	5.40	15.3	41.4	77.0 ± 0.3	−50 ± 1	95.1 ± 0.6
o-Me	4.41	13.5	35.1	99.0	56.2 ± 0.8	−46 ± 3	89.4 ± 0.7
o-Ome	11.7	32.4	83.7	216	75.8 ± 0.9	−54 ± 2	87.2 ± 0.4
o-NO_2	0.23	0.79	2.43	7.47	85.5 ± 0.5	−37 ± 2	96.4 ± 0.4
o-COOMe	0.55	1.80	5.53	17.1	84.5 ± 0.8	−34 ± 3	94.3 ± 0.6
o-Cl	1.21	3.87	11.7	34.2	82.2 ± 0.8	−35 ± 1	92.5 ± 0.4
o-Br	0.91	2.97	8.91	27.0	83.2 ± 0.7	−34 ± 2	93.1 ± 0.5
o-I	0.71	2.38	7.20	22.5	84.8 ± 0.8	−30 ± 2	93.7 ± 0.6
o-NH_2	37.8	99.9	234	576	66.1 ± 0.7	−62 ± 2	84.5 ± 0.6
(ii) Alkyl phenyl sulfides							
Et	14.4	40.5	99.0	252	69.7 ± 0.7	−58 ± 2	86.7 ± 0.5
Pr	9.27	27.0	70.2	189	73.6 ± 0.7	−48 ± 2	87.9 ± 0.5
i-Pr	11.7	33.3	89.1	243	74.2 ± 0.8	−44 ± 3	87.1 ± 0.6
t-Bu	2.88	10.2	33.3	108	72.5 ± 0.9	−45 ± 2	88.2 ± 0.7
(iii) Other sulfides							
Me_2S	30.6	77.4	198	486	67.8 ± 0.8	−58 ± 2	85.0 ± 0.6
Pr_2S	47.7	117	297	693	65.7 ± 0.7	−62 ± 2	83.9 ± 0.5
Ph_2S	5.67	16.2	48.6	126	76.7 ± 0.8	−41 ± 3	88.8 ± 0.6

unchanged, almost quantitatively. This further confirmed the absence of a free radical in the reaction pathway.

2.1.2. *Effect of substituents*

The rates of oxidation of a number of *ortho*-, *meta*- and *para*-substituted phenyl methyl sulfides, alkyl phenyl sulfides, dialkyl sulfides and diphenyl sulfide were determined at different temperatures and the activation parameters were calculated (Table 2) (Figure 2).

2.1.3. *Effect of acidity*

The reaction is catalyzed by toluene-p-sulfonic acid (TsOH) (Table 3). The TsOH dependence has the following form:

$$k_{\text{obs}} = k_2 + k_3\,[\text{TsOH}]. \tag{4}$$

The values of k_2 and k_3 are $2.53 \pm 0.09 \pm 10^{-4}\,\text{s}^{-1}$ and $4.46 \pm 0.15 \pm 10^{-4}\,\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$, respectively ($r^2 = 0.9955$).

2.1.4. *Effect of solvent*

The oxidation of methyl phenyl sulfide was studied in 19 different organic solvents. The choice of the solvent was limited by the solubility of TEACC and its reaction with primary and secondary alcohols. There was no reaction with the solvent chosen. The kinetics were similar in all the solvents. The values of k_2 are recorded in Table 4.

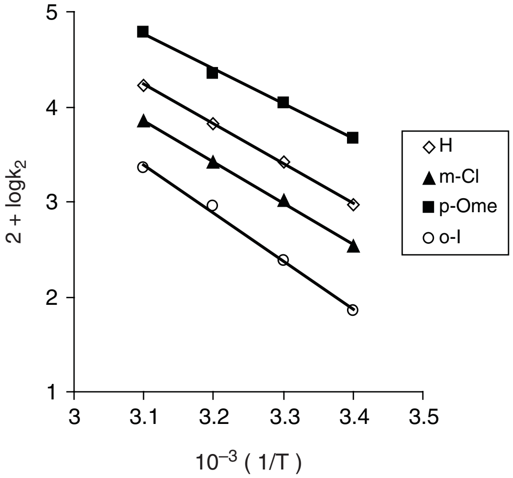


Figure 2. Oxidation of sulfides by TEACC: effect of temperature.

Table 3. Dependence of the reaction rate on hydrogen-ion concentration.

[Sulfide] 0.10 (mol dm^{-3})		[TEACC] 0.001 (mol dm^{-3})			Temperature 298 K
[TsOH] (mol dm^{-3})	0.10	0.20	0.40	0.60	0.80	1.00
$10^5\,k_{\text{obs}}$ (s^{-1})	2.97	3.51	4.32	5.04	6.03	7.11

Table 4. Solvent effect on the oxidation of MeSPh by TEACC at 308 K.

Solvent	10^4k_2 s^{-1}	Solvent	10^4k_2 s^{-1}
Chloroform	47.9	Toluene	7.94
1,2-Dichloroethane	38.9	Acetophenone	42.7
Dichloromethane	44.7	Tetrahydrofuran	14.8
DMSO	145	*t*-Butyl alcohol	18.2
Acetone	33.9	1,4-Dioxane	12.0
DMF	65.7	1,2-Dimethoxyethane	9.12
Butanone	22.4	Ethyl acetate	13.2
Nitrobenzene	51.3	Carbon disulfide	3.47
Benzene	9.77	Acetic acid	20.9
Cyclohexane	0.66		

3. Discussion

There is a fair correlation between the activation enthalpies and entropies of the oxidation of the 34 sulfides ($r^2 = 0.8819$), indicating the operation of a compensation effect (*13*). An Exner's plot (*14*) between $\log k_2$ at 288 and 318 K was linear ($r^2 = 0.9934$, slope $= 0.8336 \pm 0.0123$), indicating an excellent isokinetic relationship. The value of the isokinetic temperature evaluated from Exner's plot is 672 ± 66 K. The free energy of activation ranges from 81 to 96 kJ mol^{-1}. This variation is due to *ca.* 200 times variation in the reaction rate (Figure 3).

3.1. *Solvent effect*

The rate constants for oxidation, k_2, in 18 solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) did not exhibit a very good correlation ($R^2 = 0.8950$) in terms of the linear solvation energy relationship (5) of Kamlet *et al.* (*15*).

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha. \tag{5}$$

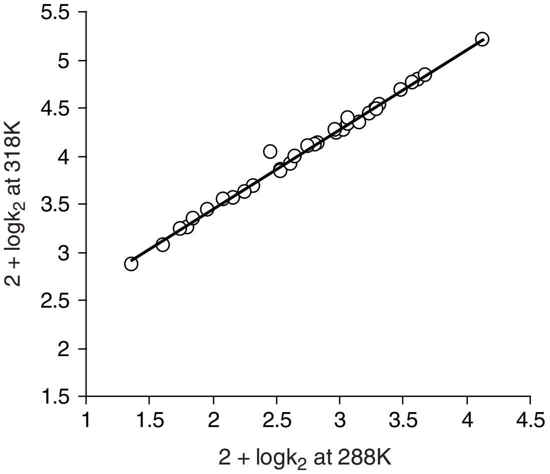


Figure 3. Exner's isokinetic relationship in the oxidation of sulfides by TEACC.

The data on the solvent effect were analyzed in terms of Swain's equation (*16*) using the cation- and anion-solvating power concept of the solvents as well.

$$\log k_2 = aA + bB + C. \tag{6}$$

Here A represents the anion-solvating power of the solvent, B the cation-solvating power and C is the intercept term. The rates in different solvents were analyzed in terms of Equation (6), separately with A and B and with $(A + B)$.

$$\log k_2 = 1.50\,(\pm 0.05)A + 1.80\,(\pm 0.04)B - 3.92, \tag{7}$$

$$R^2 = 0.9952;\ \text{sd} = 0.04;\ n = 19;\ \psi = 0.07,$$

$$\log k_2 = 1.70 \pm 0.05\,(\mathrm{A} + \mathrm{B}) - 3.71, \tag{8}$$

$$r^2 = 0.9870;\ \text{sd} = 0.06;\ n = 19;\ \psi = 0.12.$$

The rates of oxidation of methyl phenyl sulfide in different solvents show an excellent correlation with Swain's equation with both the cation- and anion-solvating powers playing significant roles, although the contribution of the cation solvation is slightly more than that of the anion solvation. However, the correlations individually with A and B were poor.

3.2. *Correlation analysis of reactivity*

The data in Table 3 show that the oxidation of different sulfides follows the order of their nucleophilicity: $Pr_2S > Me_2S > MeSPh > Ph_2S$.

3.2.1. *Aryl methyl sulfides*

The correlation of the effect of substituents on the reactivity has been widely attempted in terms of the Hammett equation (*17*) or with dual-substituent parameter (DSP) equations (*18*, *19*). In the late 1980s, Charton and Charton (*20*) introduced a triparametric *LDR* equation for the quantitative description of structural effects on chemical reactivities. This triparametric equation results from the fact that substituent types differ in their mode of electron delocalization. This difference is reflected in a different sensitivity to the electronic demand for the phenomenon being studied. It has the advantage of not requiring a choice of parameters as the same three substituent constants are reported to cover the entire range of electrical effects of substituents. We have, therefore, begun a study of structural effects on reactivity by means of the *LDR* equation. In this work, we have applied the *LDR* equation (9) to the rate constants, k_2.

$$\log k_2 = L\sigma_\mathrm{l} + D\sigma_\mathrm{d} + R\sigma_\mathrm{e} + h. \tag{9}$$

Here, σ_l is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized (resonance) electrical effect parameter when active site electronic demand is minimal and σ_e represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by Equation (10).

$$\sigma_\mathrm{D} = \eta\sigma_\mathrm{e} + \sigma_\mathrm{d}. \tag{10}$$

Here η represents the electronic demand of the reaction site and represents the ratio of regression coefficient of the sensitivity parameter, σ_e, and that of resonance parameter, σ_d, $i.e.\ \eta = R/D$. σ_D represents the delocalized electrical parameter of the diparametric *LD* equation.

Table 5. Correlation of rate of oxidation of alkyl phenyl sulfides with Pavelich–Taft equation.[a]

Temperature (K)	ρ^*	δ	R^2	sd
288	-2.80 ± 0.01	0.90 ± 0.01	0.9999	0.01
298	-2.69 ± 0.01	0.85 ± 0.01	0.9998	0.02
308	-2.61 ± 0.02	0.80 ± 0.01	0.9999	0.01
318	-2.41 ± 0.09	0.73 ± 0.02	0.9993	0.03

Note: [a]Number of data points = 5.

For *ortho*-substituted compounds, it is necessary to account for the possibility of steric effects, and Charton and Charton (*20*) therefore modified the *LDR* equation to generate the *LDRS* equation (11).

$$\log k_2 = L\sigma_\mathrm{l} + D\sigma_\mathrm{d} + R\sigma_\mathrm{e} + S\upsilon + h, \tag{11}$$

where υ is the well-known Charton's steric parameter based on Van der Waals radii (*21*).

The rates of oxidation of *ortho*-, *meta*- and *para*-substituted sulfides show excellent correlations in terms of the *LDR*/*LDRS* equations (Table 5). The values of the independent variables, σ_l, σ_d, σ_e and υ, were obtained from the work of Charton and Charton (*20*). Though the number of data points is less than the optimum number, the correlations are excellent as per Exner's (*16*) criterion also. Exner's y parameter takes into account the number of data points also.

All three regression coefficients, L, D and R, are negative indicating an electron-deficient sulfur center in the transition state of the rate-determining step. The positive value of η adds a negative increment to σ_d as in Equation (*11*), reflecting the electron-donating power of the substituent and its capacity to stabilize a cationic species.

The negative value of S indicates that the reaction is subjected to steric hindrance. This may be due to steric hindrance of the *ortho*-substituent to the approach of the oxidizing species.

To test the significance of localized, delocalized and steric effects in the *ortho*-substituted sulfides, multiple linear regression analyses were carried out with (i) σ_l, σ_d and σ_e, (ii) σ_d, σ_e and υ and (iii) σ_l, σ_e and υ. The absence of significant correlations [Equations (12)–(14)] showed that all the four substituent constants are significant.

$$\mathrm{Log}\, k_2 = -1.97(\pm 0.43)\sigma_\mathrm{l} - 1.34(\pm 0.35)\sigma_\mathrm{d} - 1.93(\pm 2.50)\sigma_\mathrm{e} - 2.90, \tag{12}$$

$$R^2 = 0.9089,\ \mathrm{sd} = 0.26,\ n = 10,\ \psi = 0.38.$$

$$\log k_2 = -1.88(\pm 0.45)\sigma_\mathrm{d} + 0.55(\pm 0.22)\sigma_\mathrm{e} - 1.74(\pm 0.56)\upsilon - 2.71, \tag{13}$$

$$R^2 = 0.8425,\ \mathrm{sd} = 0.35,\ n = 10,\ \psi = 0.47.$$

$$\log k_2 = -2.15(\pm 0.87)\sigma_\mathrm{l} - 5.36(\pm 4.37)\sigma_\mathrm{e} - 0.60(\pm 0.88)\upsilon - 2.48, \tag{14}$$

$$R^2 = 0.6781,\ \mathrm{sd} = 0.50,\ n = 10,\ \psi = 0.72.$$

Similarly, in the cases of the oxidation of *para*- and *meta*-substituted sulfides, multiple regression analyses indicated that both localization and delocalization effects are significant. There is no significant colinearity between the various substituent constants for the three series.

The percent contribution (*21* of the delocalized effect, P_D, is given by the following equation:

$$P_\mathrm{D} = \frac{|D| \times 100}{|L| + |D| + |R|}. \tag{15}$$

Similarly, the percent contribution of the steric parameter (*21*) to the total effect of the substituent, P_S, was determined by using the following equation

$$P_S = \frac{|S| \times 100}{|L| + |D| + |S| + |R|}. \tag{16}$$

The values of P_D and P_S are also recorded in Table 4. The value of P_D for the oxidation of *para*-substituted sulfides is *ca.* 56%, whereas the corresponding values for the meta- and *ortho*-substituted sulfides are *ca.* 44% and 51%, respectively. The less pronounced resonance effect from the *ortho*-position than from the *para*-position may be due to the twisting away of the methylthio group from the plane of the benzene ring.

In earlier studies on the oxidations of sulfides, involving a direct oxygen transfer via an electrophilic attack on the sulfide sulfur, the reaction constants were negative but of relatively small magnitude, *e.g.* by hydrogen peroxide (−1.13) (*22*), periodate (−1.40) (*23*), permanganate (−1.52) (*24*) and peroxydisulfate (−0.56) (*25*). Large negative reaction constants were exhibited by oxidations involving the formation of halogeno-sulfonium cations, *e.g.* by chloramine-T (−4.25) (*26*), bromine (−3.2) (*27*) and N-bromoacetamide (−3.75) (*28*). In the oxidation by N-chloroacetamide (*29*), the values of field (ρ_I) and resonance (ρ_R^+), at 298 K are −1.3 and −1.7, respectively.

3.2.2. *Alkyl phenyl sulfides*

The rates of oxidation of alkyl phenyl sulfides did not yield any significant correlation separately with Taft's σ^* or E_s values. The rates were therefore analyzed in terms of Pavelich–Taft's (*30*) DSP equation (*17*):

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0. \tag{17}$$

The correlations are excellent (Table 6). Though the number of compounds is small (five) for any analysis by a DSP equation, the results can be used qualitatively. The negative polar reaction constant confirms that the electron-donating power of the alkyl group enhances the reaction rate. The steric effect plays a minor inhibitory role.

Table 6. Temperature dependence for the reaction constants for the oxidation of organic sulfides by TEACC.

T/K	L	R	D	S	η	R^2	sd	ψ	P_D	P_S
Para-substituted										
288	−1.42 ± 0.01	−1.81 ± 0.01	−1.35 ± 0.06	–	0.69	0.9998	0.008	0.02	56.0	–
298	−1.35 ± 0.01	−1.71 ± 0.01	−1.25 ± 0.03	–	0.73	0.9999	0.005	0.01	55.9	–
308	−1.26 ± 0.01	−1.62 ± 0.01	−1.14 ± 0.03	–	0.70	0.9989	0.004	0.04	56.3	–
318	−1.17 ± 0.01	−1.52 ± 0.01	−1.10 ± 0.03	–	0.72	0.9999	0.004	0.01	56.5	–
Meta-substituted										
288	−1.80 ± 0.01	−1.42 ± 0.01	−1.29 ± 0.07	–	0.91	0.9998	0.004	0.02	44.1	–
298	−1.70 ± 0.01	−1.35 ± 0.01	−1.16 ± 0.08	–	0.87	0.9999	0.005	0.01	44.3	–
308	−1.62 ± 0.01	−1.26 ± 0.01	−1.04 ± 0.10	–	0.92	0.9998	0.007	0.02	43.8	–
318	−1.52 ± 0.01	−1.18 ± 0.01	−0.96 ± 0.07	–	0.81	0.9999	0.004	0.01	43.7	–
Ortho-substituted										
288	−1.52 ± 0.01	−1.61 ± 0.01	−1.35 ± 0.01	−1.17 ± 0.02	0.84	0.9999	0.001	0.01	51.4	27.2
298	−1.45 ± 0.01	−1.52 ± 0.01	−1.27 ± 0.01	−1.07 ± 0.02	0.84	0.9998	0.005	0.02	51.2	26.5
308	−1.34 ± 0.01	−1.45 ± 0.05	−1.15 ± 0.07	−0.99 ± 0.08	0.79	0.9989	0.008	0.05	52.0	26.2
318	−1.30 ± 0.02	−1.37 ± 0.01	−0.98 ± 0.01	−0.88 ± 0.02	0.72	0.9998	0.009	0.02	51.3	24.8

3.3. *Mechanisms*

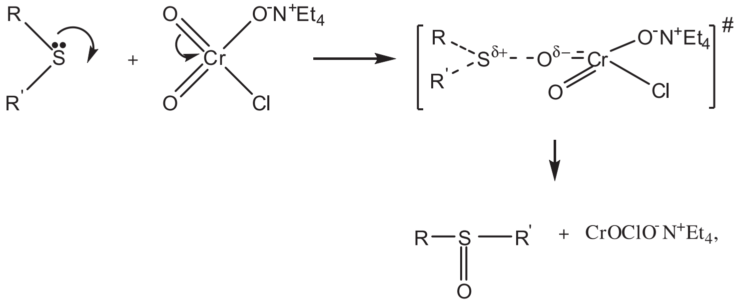
The observed dependence on TsOH suggests that the reaction follows two mechanistic pathways, one TsOH-catalyzed and the other uncatalyzed. The catalytic effect of TsOH can be attributed to a protonation of TEACC to give a stronger oxidant and electrophile (6)

$$\mathrm{O_2CrClO^-N^+Et_4 + TsOH \rightleftarrows [OCr(OH)ClO^-N^+Et_4]^+[TsO]^-}. \qquad (18)$$

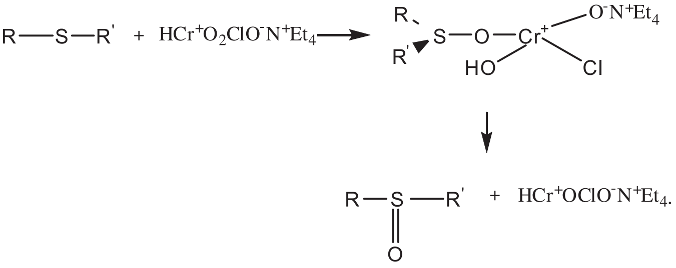
TsOH is a strong acid and is expected to be highly ionized in an aprotic polar solvent such as dimethyl sulfoxide (DMSO). However, one cannot rule out the possibility of the formation of an ion pair. Therefore, the reactive oxidizing species in the catalyzed reaction may well be the ion pair. The formation of a complex between immidazolium dichromate and TsOH has been suggested (*31*). It has been claimed that there is spectral evidence but no spectra have been included in the paper. On the basis of only a three-fold variation in [TsOH], the authors have claimed a Michaelis–Menten type of kinetics with respect to TsOH. However, a least-squares analysis of their data indicated that in that case also, the dependence on TsOH has the form $k_{\mathrm{obs}} = a + b$ [TsOH] with $a = 2.53 \pm 0.09 \times 10^{-4}\ \mathrm{s^{-1}}$, $b = 4.46 \pm 0.15 \times 10^{-4}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ and $r^2 = 0.9955$. The species could be either the protonated Cr(VI) compound or an ion pair of the protonated Cr(VI) and tosylate ion.

The analysis of the effect of solvents indicates that the transition state is more polar than the reactants. Further, the fact that both cation- and anion-solvating powers of the solvents play important roles suggests that a moderate degree of charge separation take place during the rate-determining step.

The experimental results can be accounted for in terms of rate-determining electrophilic oxygen transfer from TEACC to the sulfide:

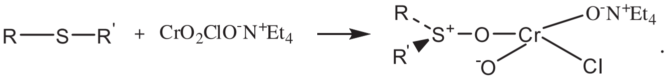


(19)



(20)

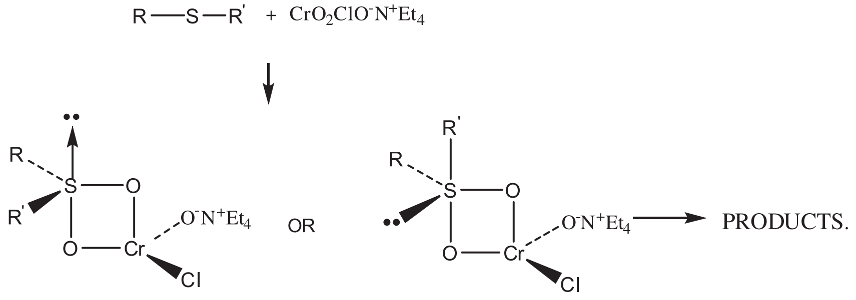
Low magnitudes of the polar reaction constants are consistent with the development of a polar transition state rather than with the formation of an intermediate with a positive sulfonium center as depicted as follows:



(21)

Further, an electrophilic attack on the sulfide sulfur is confirmed by the positive value of η which indicates that the substituent is able to stabilize a cationic or electron-deficient site. The low magnitude of η, which represents the electronic demand of the reaction, indicates a less-pronounced charge separation in the transition state. This militates against the formation of a sulfonium cation and rather supports a mechanism involving the formation of a polar transition state in the rate-determining step. The formation of a positive sulfonium cation, in the oxidation of sulfides by Cl^+ (*32*), is more responsive to steric hindrance than observed in the present study. The observed solvent effect also supports a transition state that is more polar than the reactants.

The oxidation of sulfides by TEACC may involve a cyclic intermediate as has been suggested in many reactions of Cr(VI) (*33*). The cyclic transition state will be highly strained in view of the apical position of a lone pair of electrons or an alkyl group (22).



(22)

The steric requirements of reaction (22) will be higher when compared with those of reaction (19) and the observed small magnitudes of steric reaction constants are thus consistent with the proposed acyclic mechanism. The formation of a cyclic transition state entails a more exacting specificity of orientation and should result in much larger negative entropy of activation than that observed. The value of the entropy of activation obtained in this reaction is close to the value observed in typical reactions involving oxygen transfer, *e.g.* oxidation of MeSPh by hydrogen peroxide (*23*), periodate (*24*) and PFC (*9*) ($\Delta S^* = -96, -115, -113$ and $-89\,\mathrm{J\,mol^{-1}\,K^{-1}}$, respectively). In the oxidation of vicinal diols by chromic acid, where formation of a cyclic transition state has been proposed, Chatterjee and Mukherji (*34*) obtained entropies of activation in the range of -174 to $-195\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

It is of interest to compare here the mode of oxidation of organic sulfides by PFC (*9*), PCC (*9*), PBC (*9*) and TEACC. The oxidations by PFC, PBC and TEACC presented similar kinetic pictures, *i.e.* the reactions are of first order with respect to the reductants, whereas in the oxidation by PCC, Michaelis–Menten type kinetics was observed with respect to the reductants. It is possible that the values of the formation constants for the reductant–TEACC complexes are very low. This resulted in the observation of second-order kinetics. No explanation of the difference is available presently. Solvent effects (in the oxidation by PCC, the effect of different solvents was not studied) and the dependence on TsOH are of similar nature in all these reactions, for which essentially similar mechanisms have been proposed.

4. Experimental

4.1. *Materials*

The sulfides were either commercial products or prepared by known methods (*35*) and were purified by distillation under reduced pressure or crystallization. Their purity was checked by comparing their boiling or melting points with the literature values. TEACC was prepared by the reported method (*6*). TsOH was used as a source of hydrogen ions.

4.2. *Product analysis*

MeSPh or Me_2S (0.1 mol) and TEACC (0.01 mol) was dissolved in DMSO (50 ml) and the mixture was allowed to stand for *ca*. 20 h. Most of the solvent was removed under reduced pressure. The residue was diluted with water and extracted with chloroform (3 × 50 ml). The chloroform layer was dried over anhydrous magnesium sulfate, the solvent was removed by evaporation and the residue was analyzed by IR and ^1H NMR spectroscopy. The spectra were identical with those of the corresponding sulfoxides. Peaks characteristic of the sulfide and sulfone could not be detected. In IR spectra, the product showed a strong and broad absorption at $1050\,cm^{-1}$. No band either at 1330 or $1135\,cm^{-1}$, characteristic of sulfones (*36*), was seen. In NMR spectroscopy, studied in the case of Me_2S, the peak due to methyl protons shifted from 2.1 ppm, in the sulfide, to 2.6 ppm in the product. In the corresponding sulfone, the peak should have appeared at 3.0 ppm (*37*). Similar experiments were performed with other sulfides also. In all cases, the products were the corresponding sulfoxides. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method, was 3.90 ± 0.15.

4.3. *Kinetic measurements*

The solvent was DMSO, unless mentioned otherwise. The reactions were studied at constant temperature (±0.1 K) and were followed by monitoring the decrease in the concentration of TEACC at 370 nm for up to 80% of the extent of the reaction. Duplicate kinetic runs showed that the rate constants are reproducible to within ±3%. All kinetic runs, except those for studying the effect of acidity, were studied in the absence of TsOH. The values of the second-order rate constants were computed from the relation $k_2 = k_{obs}/[\text{sulfide}]$. Simple and multivariate regression analyses were carried out by the least-squares method.

Acknowledgements

Thanks are due to the University Grants Commission, New Delhi, India, for financial support in the form of a Major Research project and to Professor Kalyan Banerji, Dean, Sciences, NLU, Mandore, Jodhpur (India).

References

(1) Corey, E.J.; Suggs, W.J. *Tetrahedron Lett*. **1975,** *31,* 2647–2650.
(2) Guziec, F.S.; Luzio, F.A. *Synthesis* **1980,** *9,* 691–694.
(3) Bhattacharjee, M.N.; Choudhuri, M.K.; Dasgupta, H.S.; Roy, N.; Khathing, D.T. *Synthesis* **1982,** *7,* 588–590.
(4) Balasubramanian, K.; Prathiba, V. *Indian J. Chem*. **1986,** *25B,* 326–327.
(5) Pandurangan, A.; Murugesan, V.; Palanichamy, M. *J. Indian Chem. Soc.* **1995,** *72,* 479–480.
(6) Pandurangan, A.; Murugesan, V. *J. Indian Chem. Soc.* **1996,** *73,* 484–486.
(7) Swami, P.; Yajurvedi, D.; Mishra, P.; Sharma, P.K. *Int. J. Chem. Kinet*. **2010,** *42,* 50–55.
(8) Vadera, K.; Yajurvedi, D.; Purohit, P.; Mishra, P.; Sharma, P.K. *Prog. React. Kinet. Mech.* **2010,** *35,* 265–280.
(9) [a] Banerji, K.K. *J. Chem. Soc., Perkin Trans* **1988,** *2,* 2065–2069; [b] Panigrahi, G.P.; Mahapatro, D.D. *Int J. Chem. Kinet*. **1981,** *13,* 85–96; [c] Loonkar, K.; Sharma, P.K.; Banerji, K.K. *J. Chem Res.* [S] **1997,** *194,* [M] 1262–1285.

(10) Karunakaran, C.; Venkataraman, R.; Kamalam, R. *Monatsh. Chem.* **1999,** *130,* 1461–1470.
(11) Brown, H.C.; Rao, C.G.; Kulkarni, S.U. *J. Org. Chem.* **1979,** *44,* 2809–2810.
(12) Bhattacharjee, M.N.; Choudhuri, M.K.; Purakayastha, S. *Tetrahedron* **1987,** *43,* 5389–5392.
(13) Liu, L.; Guo, Q.-X. *Chem. Rev.* **2001,** *101,* 673–696.
(14) Exner, O. *Collect. Czech. Chem. Commun.* **1964,** *29,* 1094–1102.
(15) Kamlet, M.J.; Abboud, J.L.M.; Abraham, M.H.; Taft, R.W. *J. Org. Chem.* **1983,** *48,* 2877–2887.
(16) Swain, C.G.; Swain, M.S.; Powel, A.L.; Alunni, S. *J. Am. Chem. Soc.* **1983,** *105,* 502–513.
(17) Johnson, C.D. *The Hammett Equation*; University Press: Cambridge, 1973; Vol. 78, pp 441–459.
(18) Dayal, S.K.; Ehrenson, S.; Taft, R.W. *J. Am. Chem. Soc.* **1974,** *94,* 9113–9117.
(19) Swain, C.G.; Unger, S.H.; Rosenquest, N.R.; Swain, M.S. *J. Am. Chem. Soc.* **1983,** *105,* 492–502.
(20) Charton, M.; Charton, B. *Bull. Soc. Chim. Fr.* **1988,** *199,* 441–459 and references cited therein.
(21) Charton, M. *J. Org. Chem.* **1975,** *40,* 407–411.
(22) Modena, G.; Maioli, L. *Gazz. Chim. Ital*. **1957,** *87,* 1306–1312.
(23) Ruff, F.; Kucsman, A. *J. Chem. Soc., Perkin Trans.* **1985,** *2,* 683–687.
(24) Banerji, K.K. *Tetrahedron* **1988,** *44,* 2969–2975.
(25) Srinivasan, C.; Kuthalingam, P.; Arumugam, N. *Can. J. Chem.* **1978,** *56,* 3043–3046.
(26) Ruff, F.; Kucsman, A. *J. Chem. Soc., Perkin Trans.* **1975,** *2,* 509–519.
(27) Miotti, U.; Modena, G.; Sadea, L. *J. Chem. Soc. B* **1975,** 802–811.
(28) Perumal, S.; Alagumalai, S.; Selvaraj, S.; Arumugam, N. *Tetrahedron* **1986,** *42,* 4867–4873.
(29) Agarwal, A.; Bhatt, P.; Banerji, K.K. *J. Phys. Org. Chem.* **1990,** *3,* 174–180.
(30) Pavelich, W.H.; Taft, R.W. *J. Am. Chem. Soc.* **1956,** *79,* 4935–4940.
(31) Karunakaran, C.; Chidambarnathan, V. *Oxid. Commun.* **1998,** *21,* 381–387.
(32) Ruff, F.; Kapovits, I.; Rabai, J.; Kucsman, A. *Tetrahedron* **1978,** *34,* 2767–2774.
(33) Chang, Y.W.; Westheimer, F.H. *J. Am. Chem. Soc.* **1960,** *82,* 1401–1405; Rocek, J.; Westheimer, F.H. *J. Am. Chem. Soc.* **1962,** *84,* 2241–2246.
(34) Chatterjee, A.C.; Mukherji, S.K. *Z. Phys. Chem.* **1957,** *207,* 372–378; **1958,** *208,* 281–288; **1959,** *209,* 166–171.
(35) Zuncke, T.; Swartz, H. *Chem. Ber*. **1913,** *46,* 775–783; **1915,** *48,* 1242–1251; Hofmann, A.W. *Chem. Ber.* **1887,** *20,* 2260–2268; Gilman, H.; Gainer, G.C. *J. Am. Chem. Soc.* **1949,** *71,* 1747–1751; Saggiomo, A.L.; Craig, P.N.; Gordon, M.J. *J. Org. Chem.* **1958,** *23,* 1906–1909; Nodiff, E.A.; Lipschutz, S.; Craig, P.N.; Gordon, M.J. *J. Org. Chem.* **1960,** *25,* 60–65.
(36) Pouchart, C.J. *The Aldrich Library of IR Spectra*, 3rd ed.; Sigma-Aldrich Corp.: St. Louis, MO, 1981.
(37) Pouchart, C.J. *The Aldrich Library of NMR Spectra*, 1st and 2nd ed.; Sigma-Aldrich Corp.: St. Louis, MO, 1983.